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Defence Science and  
Technology Organisation

# Personnel Exposure to Airborne Isocyanates and Solvents During Shipboard Painting with 2-Pack Polyurethane Paints

*J. Kibby\*, G. DeNola#, P. J. Hanhela# and W. Mazurek#*

**\*On contract to DSTO**

**#Maritime Platforms Division**

Defence Science and Technology Organisation

DSTO-TR-2228

## **ABSTRACT**

Shipboard and laboratory trials were conducted to determine personnel exposure to airborne solvents and isocyanates during the application, by roller and brush, of 2-pack polyurethane paints. Airborne concentrations in the breathing zones of the operators were found to be <1/200th (<0.1  $\mu\text{g}/\text{m}^3$ ) of the 8 h time-weighted average (TWA) exposure limits for isocyanates during the application of Interthane 987 LSALGP and Interthane 864 LSANSP on a RAN vessel, in the open air, on a hot day with a slight wind. Similarly, brush and roller application of the paints in a simulated enclosed space produced airborne isocyanate concentrations <3  $\mu\text{g}/\text{m}^3$ . The dust produced during light sanding of the polyurethane paint, 24 h after curing, did not show quantifiable levels (<0.1  $\mu\text{g}/\text{m}^3$ ) of isocyanates. Although it appeared that respiratory protection from airborne isocyanates was not required with brush/roller applications, personnel should be protected from dermal exposure to the liquid paints. There appeared to be a greater risk from paint solvent respiratory exposure than from airborne isocyanates.

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# Personnel Exposure to Airborne Isocyanates and Solvents During Shipboard Painting with 2-Pack Polyurethane Paints

## Executive Summary

At the request of the Executive Director of SHIPSAFE, a study was undertaken to determine the exposure of painters to airborne isocyanates and solvents during brush/roller application of 2-pack polyurethane paints (Interthane 987 LSALGP and Interthane 864 LSANSP).

A shipboard trial was undertaken where the paints were applied to the decks of a RAN vessel, in dry dock in Darwin. Laboratory trials were also conducted to simulate an enclosed environment at tropical ambient temperatures and to complement the shipboard trials.

Isocyanate vapour and aerosols were monitored close to the substrate surface (10 cm) during painting in a simulated enclosed environment and in the breathing zone during shipboard application at ambient air temperatures of 30°C – 35°C and substrate temperatures of 55°C. In neither case did the isocyanate concentrations exceed the Time-Weighted (8 h) exposure limits (TWA). During the shipboard painting trial the airborne isocyanate concentrations were found to be  $<1/200^{\text{th}}$  ( $<0.1 \mu\text{g}/\text{m}^3$ ) of the TWA.

Solvent vapour concentrations were also found to be below the TWA but these levels may be exceeded under conditions of elevated ambient temperatures and poor ventilation.

After curing for 24 h, the painted surface was sanded lightly. Analysis of the airborne dust indicated isocyanate concentrations below the level of detection.

The results show that during brush/roller application of polyurethane paints, respiratory protection for isocyanates is not required under the conditions studied. However, adequate ventilation is required for personnel protection from solvent vapours. Personnel protective equipment should be worn for protection against skin contact with the liquid paint.

# Authors

## **J. Kibby,** Maritime Platforms Division

*Jeffery Kibby was employed as a contractor for DSTO. He had previously worked for ICI, Waters and Scope Consulting as a senior analytical chemist and a manager. He holds a PhD in organic chemistry and has had post-doctoral experience in the USA.*

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## **G. DeNola** Maritime Platforms Division

*Georgio DeNola has had extensive experience in paint technology and in mass spectrometry-gas chromatography. He has worked in air quality research at DSTO for the past 10 years. He holds a degree in chemistry from the University of Victoria and a post graduate degree in Toxicology from RMIT University.*

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## **P.J. Hanhela** Maritime Platforms Division

*Peter Hanhela has extensive experience in organic, analytical and polymer chemistry. During the past 15 years he has specialised in air analysis. Peter has published extensively. He holds a Diploma of Applied chemistry from Victoria University (Footscray Institute of Technology)*

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## **W. Mazurek** Maritime Platforms Division

*Waldemar Mazurek is a Principal Research Scientist with extensive experience in organic, inorganic and analytical chemistry. He has also had several years experience in paint technology. During the past 15 years he has developed expertise in air quality monitoring in enclosed environments such as submarines, military aircraft and armoured vehicles.*

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# 1. Introduction

A recent Australian study has shown that isocyanates to be the third largest contributing occupational source of asthma (after wood dust and unspecified dust) [1]. Polyurethane paints are a major source of exposure to isocyanates [2]. These paints contain low volatility isocyanate prepolymers in addition to small quantities of volatile isocyanate monomers [2,3]. The monomers may become airborne as vapour whilst the non-volatile prepolymers and partially cured oligomers may form aerosols during spray painting and sanding of the painted surface. Because of their reactivity, airborne isocyanates can irritate the respiratory tract and may result in asthma attacks either immediately or some hours after exposure [4,5]. Repeated exposures may result in impairment of lung function. Personnel may also become sensitised to isocyanates at concentrations below the maximum exposure limits [6]. For these reasons there are strict controls on occupational exposure to airborne isocyanates. This is largely achieved by the manufacturer ensuring that the free (unreacted) isocyanate in the paint is kept to a minimum [7]. However, even though respiratory exposure to isocyanate monomers are very low or non-detectable, isocyanate -induced asthma continues to be a problem as long as skin exposure occurs [8]. Thus, it has been suggested that dermal exposure contributes to isocyanate sensitisation and asthma.

During paint spraying, the low volatility isocyanates become airborne as aerosols in addition to the vaporisation of the volatile unreacted isocyanate monomers. However, during brush/roller applications there is less opportunity for the generation of aerosols and the principal source of airborne isocyanates will be the small quantities of volatile monomeric species present in the paint.

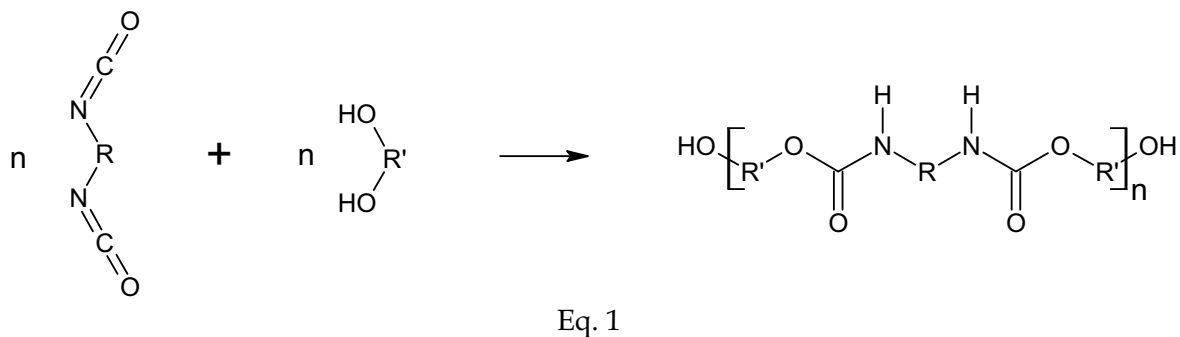
Sanding of cured polyurethane paints can also result in personnel exposure to isocyanates, both dermal and respiratory. This is due to the slow formation of the polymer film with the unreacted isocyanate groups being detected for prolonged periods (days and weeks) [8].

Polyurethane paints have wide application in the Australian Defence Forces (ADF) and industry. There are guidelines for personnel protection during the spray painting of polyurethanes [9-12]. Within the ADF, the extent of personnel protection required during brush/roller application is unclear [13,14]. However, general industrial applications require wearing of appropriate personnel protective equipment to avoid skin contact and ensuring good ventilation without specifically requiring the use of respirators [10-12]. These recommendations may not address the potential effects of elevated ambient and substrate temperatures on airborne isocyanate concentrations. Such conditions are generally experienced during the painting of Royal Australian Navy (RAN) vessels in northern Australia. Although it is important to provide the painter with protection from potentially adverse health effects of isocyanates, burdensome respirators should not be imposed unnecessarily, particularly in hot and humid climatic conditions. However, the RAN has sought reassurance that the current brush/roller painting practices do not pose a health risk to painters [13].

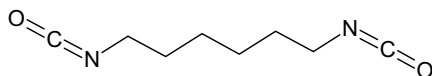
## 1.1 Polyurethane Chemistry

In this study two paints were of interest to the RAN, the low gloss Interthane 987 and the non-skid Interthane 864. According to the information provided by the manufacturer the Part B packs contain the curing agent (Material Safety Data Sheet, Interthane 990 Part B [15], Interthane 864-863 NSP Curing Agent [16]) with <1 % monomeric isocyanate (hexamethylene diisocyanate, HDI) (1) [7].

Polyurethane 2-pack paints, when mixed, cure by the reaction of a polyalcohol with a diisocyanate to form a urethane polymer (eq. 1):



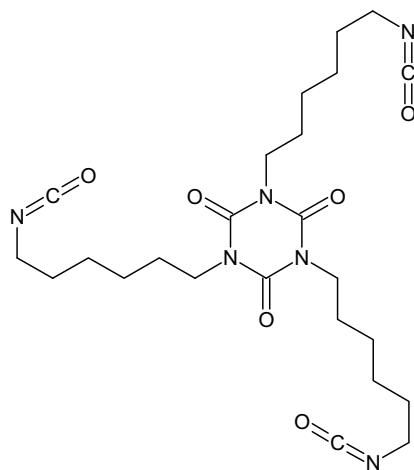
Most of the isocyanates is expected to be present as the less volatile oligomers such as the isocyanurate trimer (2) and pentamer (3) with the trimer being the predominant isocyanate species [7,17,18]. Figure 1 shows the gel permeation chromatogram of HDI oligomers from a commercial formulation. The dominance of the trimer is apparent with the pentamer and heptamer, etc. present in progressively lower concentrations.



1

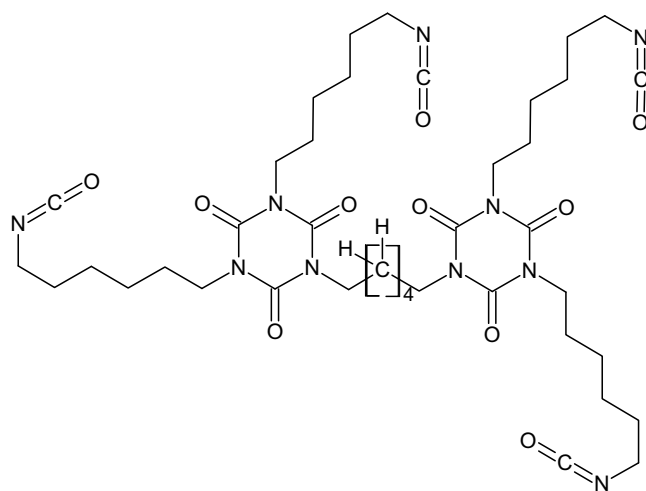
HDI Monomer

(Vapour Pressure at 20°C, 1.1x10<sup>-2</sup> mmHg, [18])



2

HDI Isocyanurate Trimer  
(Vapour Pressure at 20°C,  $5.2 \times 10^{-9}$  mmHg, [18])



3

HDI Isocyanurate Pentamer



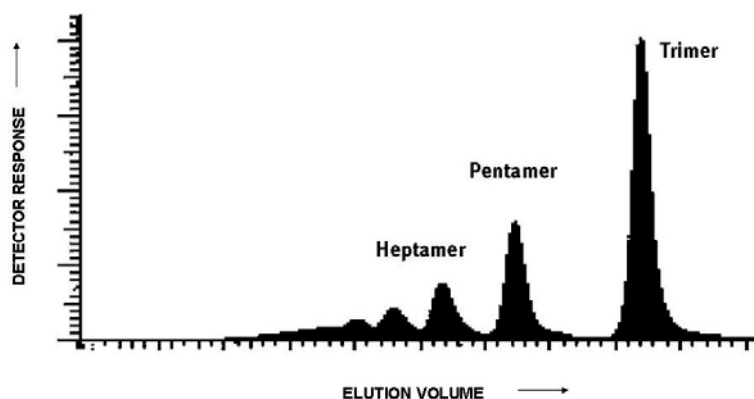


Figure 1: Gel Permeation Chromatogram of HDI oligomers from a commercial paint formulation (reproduced from ref. 17)

The respiratory exposure to isocyanates from these paints was assessed during brush/roller application under tropical conditions on steel plate surfaces. In addition, an assessment was made of the exposure to isocyanates from the dust produced during sanding of the cured polyurethane paint.

A study of brush and roller application of isocyanate paints to a car door and at UK petrol stations showed that airborne isocyanate concentrations were below the limit of detection ( $0.01 \mu\text{g}/\text{m}^3$ ) [19]. Although ambient temperatures were not provided, given the geographic location it is unlikely that they approached those of tropical Australia.

In addition to the potential health hazards posed by the isocyanates, the effects of solvent vapours also need to be taken into consideration. Studies of male painters exposed to white spirits (40 ppm) and toluene showed that they were significantly impaired on tests of memory, reaction time, psychomotor coordination and concept formation [20, 21]. There is also a risk of developing chronic toxic encephalopathy on occupational exposure to solvents and the risk to neuropsychiatric disease has been estimated to develop after chronic exposure to 100 ppm white spirits [22].

## 1.2 Exposure Limits

### 1.2.1 Isocyanates

The Australian National Occupational Health and Safety Commission (NOHSC) [23] and the UK Health and Safety Executive (HSE) have set an 8-h time-weighted exposure limit (TWA) of  $20 \mu\text{g}/\text{m}^3$  [11] based on the Total Reactive Isocyanate Groups (TRIG) which encompasses all the isocyanate-terminated compounds including oligomers (aerosols). The American Conference of Government and Industrial Hygienists (ACGIH) [24] and the US National Institute for Occupational Safety and Health (NIOSH) [25] specify individual isocyanates with a TWA for airborne HDI vapour at  $35 \mu\text{g}/\text{m}^3$  (0.005 ppm).

### 1.2.2 Solvents

The paints under consideration contained solvents consisting of aromatics, ketones and esters according to the Material Safety Data Sheet (Table 1) [26]. The exposure limits of two of the solvents (cyclohexanone and light aromatic solvent naphtha) are relatively low and could be exceeded in poorly ventilated areas.

## 1.3 Paint Application

During the application of polyurethane paints, personnel exposure to isocyanates and solvent vapours may occur through the evaporation of solvents and HDI from the open paint cans and during application by brush/roller or spray (Fig. 2). Emissions from the paint cans are likely to be low because of the small surface area of the liquid paint and particularly after the two components are mixed allowing the HDI monomer to react. The surface area of the paint is significantly increased on application of the paint which greatly enhances evaporation of both the solvents and unreacted HDI monomer. Significantly higher quantities of airborne solvents and isocyanates are likely to be generated during spray application, both in the form of vapours and aerosols. However, this study is concerned with brush/roller application where airborne emissions are likely to be restricted to solvent and HDI vapours.

In addition to paint handling and application there is also a potential for exposure to partially reacted, airborne isocyanates (solid aerosols) during sanding of an incompletely cured paint.

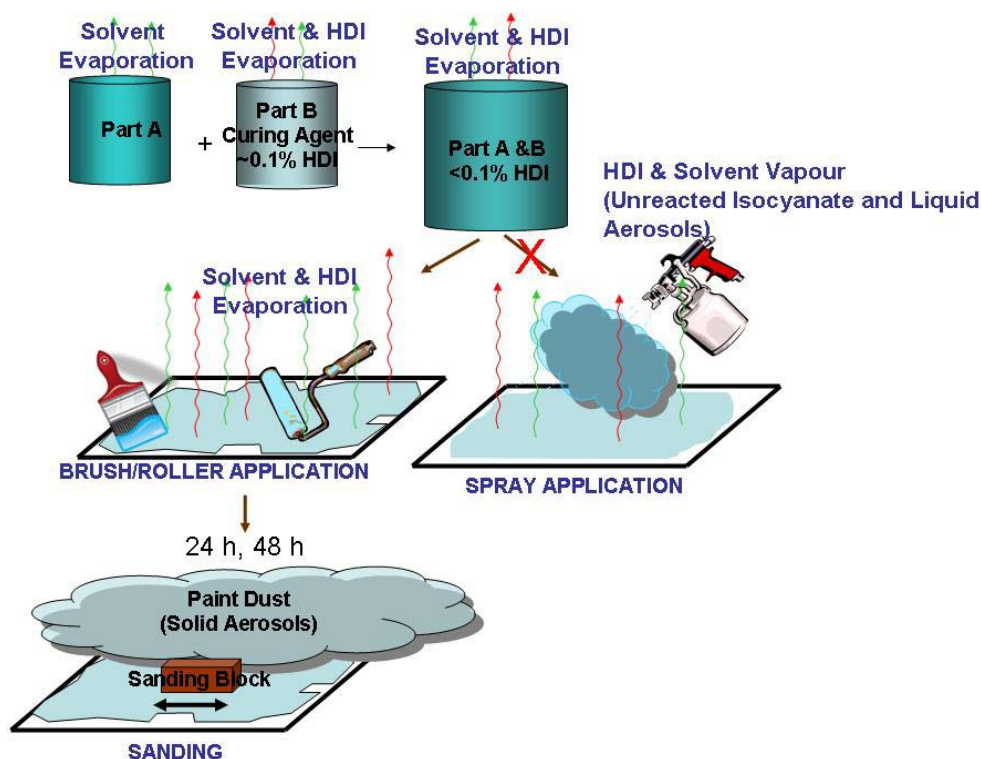


Figure 2: Schematic diagram showing the stages of application of polyurethanes and emissions to air

Table 1: Major Solvent Components and Maximum Exposure Levels for Interthane 987 and Interthane 864 Paints [26]

Solvent <sup>a</sup>	Boiling Point (°C)	Interthane 987 LSALGP	Interthane 864 LSANSP	TWA (NOHSC) [23]
<b>Part A</b>				
Cyclohexanone	155.6	-	2.5-10%	25ppm (100 mg/m <sup>3</sup> )
Light Aromatic Solvent Naphtha	100-213	10-25%	10-25%	50 ppm <sup>b</sup>
Xylene	137-140	10-25%		80 ppm (350 mg/m <sup>3</sup> )
<b>Part B</b>				
n-Butyl Acetate	97.8	2.5-10%	2.5-10%	150ppm (713 mg/m <sup>3</sup> )
Light Aromatic Solvent Naphtha	100-213	10-25%	10-25%-	50ppm <sup>b</sup>

<sup>a</sup>Symptoms for acute exposure for these solvents include eye, skin and respiratory irritations [24-27];

<sup>b</sup>ACGIH [24].

## 2. Aims

Specifically, this report sets out to address the Statement of Requirement of the SHIPSAFE Board, with regard to shipboard painting with isocyanate paints, by the following means:

- determining if there is excessive human exposure to isocyanates from two-pack polyurethane paints (PUP) during mixing and application by brush or roller, to ship superstructures, in an open-air environment in tropical Australia,
- providing an assessment of the levels of exposure that can be expected by personnel applying the paints,
- measuring the airborne concentrations of polyisocyanates (aerosol) and diisocyanate (vapour) when removing cured paint (between 24 h and 14 days old) by mechanical abrasion.
- measuring airborne concentrations of solvents during brush/roller paint application.

## 3. Experimental

### 3.1 Paints

The following paint systems were used:

1. Superstructure coating; Interthane 987 LSALGP (Low Gloss Paint) Part A (PLA297)/ Interthane (990) 987 Curing Agent, Part B (PHA046)
2. Non Skid Deck coating; Interthane (Pewter) 864 LSANSP (Non-Slip Paint) Part A (PLA786)/ Interthane 864 NSP HP, Part B (PLA047)

### 3.2 Analytical Standards

Hexamethylene diisocyanate derivatives of 9-(N-methylaminomethyl) anthracene (MAMA) and methoxy-2-phenyl-1-piperazine (MOPIP) were prepared according to the Occupational Safety and Health Agency (OSHA, US) Method 42 [28], itself a modified method from Goldberg *et al* [29]. MAMA (4) and MOPIP (5) were obtained from Aldrich, with a purity of 99%, 98%, respectively and HDI (1), of an unknown purity, was obtained from Sigma.  $d_8$ -Toluene was used for air analysis and was obtained from Aldrich.

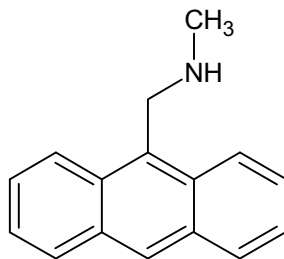
### 3.3 Air Sampling

#### 3.3.1 Isocyanates

A 2-stage filter sampler was used, with the first stage designed to trap the aerosols and the second stage for the vapours in accordance with American Society for Testing and Materials (ASTM) Standard Test Method D 6562-00 [30] and D6561-00 [31] for isocyanates (monomer and oligomers respectively). A 37 mm SKC preloaded cassette was used with twin filters (Omega Instrument Company, ISO-CHEK<sup>®</sup>, 37 mm, Dual Filter, 225-9022A) containing a polytetrafluoroethylene (PTFE) top filter and a lower glass fibre filter impregnated with 9-(N-methylaminomethyl)anthracene (MAMA).

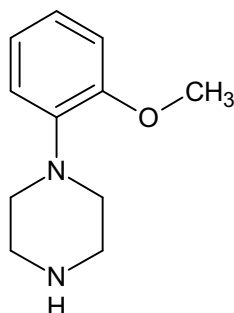
The total sampling time was 15 min giving a total of 15 L of air sampled at flow rates of 1 L/min. The results were adjusted for 8 h (TWA) exposures.

Air sampling for peak exposure levels was conducted at a flow rate of 3 L/min. for 5 min with a limited number of samples. This was the highest attainable flow with a low risk of separating the top filter. This was done to discern whether the HDI monomer was present during the first 5 min of application or if it persisted throughout the entire sampling time.



4  
MAMA

9-(N-methylaminomethyl)anthracene



5  
MOPIP

Methoxy-2-phenyl-1-piperazine

### 3.3.2 Airborne Solvent Concentrations

Whole air samples were collected in 1 L electro-passivated stainless steel canisters (Scientific Instruments Specialists, Graseby Andersen, USA).

Changes in solvent vapour concentrations were measured using a ppbRae photo-ionisation detector (RAE Systems, USA) calibrated with iso-butylene. The concentrations of the individual solvents were determined from the analysis of canister whole air samples corresponding to the PID readings. The air samples were analysed by GC-MS.

## 3.4 Chemical Analyses

### 3.4.1 Isocyanate Monomer Content of Interthane (990) 987 Curing Agent Part B (PHA046)

To 0.1 g of Interthane 990 Curing Agent in 5 mL of dry tetrahydrofuran (THF) in a 50 mL volumetric flask was added 0.1 g of MOPIP in 5 mL dry THF. The mixture was allowed to stand at room temperature for 2 h. Dimethylformamide was then added to the mark and

aliquots of the resultant solution analysed by HPLC using fluorescence detection (Excitation wavelength: 254 nm; Emission wavelength: 412 nm).

The High Performance Liquid Chromatography (HPLC) system was calibrated with working standard solutions (in the range 0-250  $\mu\text{g/mL}$ ) prepared from the MOPIP urea derivative of HDI, (m.p. 198-200°C) [30].

### 3.4.2 Analysis of Filter Samples

The filter sampling system (Fig. 3) allowed the simultaneous collection (in the one filter cassette) of airborne isocyanates in aerosol (a) and vapour (b) form using the following standard procedures [30].

(a) The vapour fraction was collected on a glass fibre filter impregnated with MAMA. Trapped HDI urea derivatives were desorbed with a mixture containing dimethylformamide/acetonitrile/triethylammonium phosphate buffer and analysed by reversed phase high performance liquid chromatography (HPLC) with fluorescence detection [30].

(b) The aerosol fraction was collected on a polytetrafluoroethylene (PTFE) filter. Immediately after sampling, the filter was transferred into a jar containing a 5 mL solution of MOPIP in toluene (0.1 mg/mL). The toluene was evaporated and the residue dissolved in acetonitrile containing 0.5% acetic anhydride. The resulting solution was analysed by reversed phase HPLC, using gradient elution with fluorescence detection [31].



Figure 3: Iso-Check "Complete Isocyanate Sampling System" for isocyanate vapour and aerosols

### 3.4.3 Analysis of Canister Air Samples

Solvent air concentrations were determined by concentrating the canister air samples on an Entech 7100 preconcentrator followed by analysis with an Agilent Gas Chromatograph (CG, 6890)/mass spectrometer (MSD, 5943). The GC transfer and the sample transfer lines were set at 100°C with the heated block set at 80°C. An internally produced d<sub>8</sub>-toluene standard was added to the sample for quantification. Preconcentrator trap parameters are listed in Table 2.

Table 2: Preconcentrator Trap (Cold Trap Dehydration Mode)

	Trap 1	Trap 2	Trap 3
<b>Temperatures</b>	-10°C	-50°C	-150°C
<b>Preheat</b>	10°C	50°C	
<b>Desorb</b>	10°C	180°C (4 min)	~80°C
<b>Bake</b>	150°C (5min)	190°C (auto)	5 min
<b>Inject</b>			2 min

The chromatography was carried out using a DB-5 60 m x 0.32 mm x 1 µm capillary column using helium as the carrier gas at 1.5 mL/min. The temperature program of the oven was 35°C held for 2 min, ramped to 110°C at 10°C/min, 150°C at 5°C/min, 2°C/min and 225°C for 5 min. Centroid data was collected with 0.25 sec scan time and 0.05 sec interscan delay.

### 3.5 Painting Trial, HMAS CESSNOCK,



Figure 4: Painting trial, HMAS CESSNOCK, Darwin, showing locations of air sampling of personnel and down wind



The trial was conducted aboard the decommissioned HMAS CESSNOCK, (Darwin, 23 August, 2005) in the dry dock at Fleet Intermediate Maintenance Activity (FIMA), Darwin, Larrakeyah Barracks. Two FIMA personnel were fitted with an Aircheck 2000 personal sampling pumps and air sampling filters were placed in their breathing zone (Fig. 4). Additional air sampling was also conducted at the following positions:

- (1) downwind of the painting (~70 cm above the deck),
- (2) above the painted deck in the operator breathing zone (~70 cm above the deck) and
- (3) above the paint pot (~40 cm).

The ambient air temperature was 43°C in the sun and 33°C in the shade with a deck temperature of 57°C. The wind speed was estimated to be 2.5 – 4 m/s as measured with an air velocity meter (VelociCalc Plus, TSI). FIMA personnel indicated that they regularly paint under these conditions. The surface area painted was approximately 25 m<sup>2</sup>.

## 3.6 Laboratory Trials

### 3.6.1 Enclosed Space

Emissions from the paints were determined in the laboratory under conditions of elevated temperatures and poor ventilation. A test bed was setup in a fume cupboard (approx. 1 m<sup>3</sup>) to allow adequate ventilation before and after the experiment while maintaining a confined volume during painting.

An aluminum plate (650 mm x 650 mm x 13 mm) was maintained at a surface temperature of 50°C while resting on three thermostated hotplates (BTL Thermoplate, Industrial Equipment and Control Pty. Ltd. Cat No. 2092.001) and irradiated (from above) by two 250 W reflector light globes (Fig. 5). The air temperature in the enclosure was 30°C. A film of Melinex<sup>®</sup> polyester (50 µm, 700 mm x 550 mm) was placed over the aluminum plate.

The paints were mixed in accordance to the manufacturer's requirements. The paints were applied to the polyester surface with a paint roller to an average dry thickness of approximately 300 µm (Interthane 987, LSA- Low Gloss Paint) and 800 µm (Interthane 864, LSA-Non-Slip Paint). The manufacturer's recommended dry paint thicknesses were 50-75 µm for spray application and 400 µm for brush application [32,33]. The high film thickness for brush/roller application was expected to enhance emissions of isocyanates from the coating surface due to the higher cross-sectional area. Air sampling was conducted approximately 7.5 cm above the paint surface

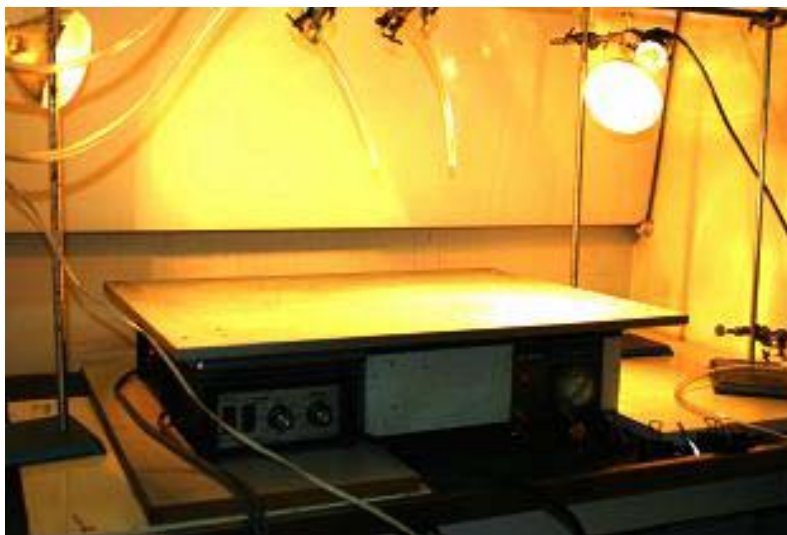


Figure 5: Laboratory trials simulating painting in an enclosed space with air temperature of 30°C and surface temperature of 55°C

### 3.6.2 Open Space, Outdoors

Isocyanate monitoring was also conducted outdoors at Defence Science and Technology Organisation (DSTO), Maribyrnong. The paint (Interthane 987 LSALGP) was applied with a roller to the polyester sheet (*vide supra*) on a heated aluminum plate (*vide supra*) with the surface temperature maintained at 55°C. Air sampling was conducted 7.5 cm and 75 cm above the paint surface with an air temperature of 20°C and wind speed of 1 m/sec.

## 3.7 Air Monitoring for Isocyanates after Sanding

The two paints were applied to a polyester sheet (Melinex<sup>®</sup>) by roller and allowed to cure for 24 h. The surface was sanded lightly, by hand. The edges were folded inward to form a bag and an air sample (15 L) was taken within the bag to maximize the concentration of any trapped isocyanate vapour.

## 4. Results

### 4.1 Isocyanates

The Limit of Detection (LOD) of  $0.03 \mu\text{g}/\text{m}^3$ , for the analysis was defined as isocyanate concentration corresponding to 3 times the peak height over the interfering peaks of a blank sample and the Limit of Quantitation (LOQ),  $0.1 \mu\text{g}/\text{m}^3$ , was based on the isocyanate concentration corresponding to 9 times greater than the peak height over the interfering peaks of a blank sample [34].

Liquid Interthane 987 Curing Agent Part B (PHA046), Batch No. DL3781AB (Akzo Nobel Pty Ltd), was analysed for HDI monomer and found to contain 0.15% HDI. The product label indicated a concentration of <0.4%.

Airborne isocyanate concentrations were monitored for aerosols (oligomers) and vapours (HDI) using 2-stage filter cassettes. However, in all cases, only HDI was detected. During the trial undertaken aboard HMAS CESSNOCK, personnel were fitted with air sampling devices in the breathing zone under conditions of relatively high ambient temperatures (surface and air) and low wind speeds which would be conducive to the volatilisation of the free isocyanate monomer from the painted surface. Despite these conditions the concentrations of airborne isocyanates were below the level of quantitation ( $<0.1 \mu\text{g}/\text{m}^3$ , Table 2).

Three measurements were undertaken at shorter sampling times (5, 12 min.) in order to capture initial (peak) concentrations. Although these gave higher concentrations of total airborne isocyanate concentrations, the values were still well below (1/10) the maximum allowable exposure limit at 10 cm above the painted surface.

Measurements of airborne isocyanate concentrations were made 7.5 cm above the paint pot (containing premixed paint) and were found to be below the level of quantitation. However, concentrations in the range  $0.6 - 2.7 \mu\text{g}/\text{m}^3$  were obtained above the freshly painted surface at an air temperature of  $30^\circ\text{C}$  and surface temperature of  $55^\circ\text{C}$ .

When Part B (the curing agent-containing component) was applied to the surface under the above conditions, the airborne isocyanate concentrations measured 10 cm above the paint surface were substantially higher ( $5.2, 7.9 \mu\text{g}/\text{m}^3$ ) than for the premixed paint. This indicated that a significant amount of the monomeric isocyanate had reacted during the mixing of the 2 packs prior to application.

The experiments were repeated at DSTO in outdoor conditions with roller application of the paint. The results showed very low isocyanate concentrations (below the quantitation limit) just above the surface (7.5 cm) and in the breathing zone of an applicator (70 cm above the paint surface). These measurements correlated well with the data from the shipboard trial despite the differences in air temperatures ( $20^\circ\text{C}$  versus  $43^\circ\text{C}$ ).

Painting conditions without ventilation in an enclosed space and elevated temperatures were simulated in laboratory trials and air samples were taken above the surface of the paint pot

(Table 3). Although these conditions were extreme and not recommended in practice without adequate respiratory protection, the airborne isocyanate concentrations were found to be substantially below the maximum allowable concentrations ( $20 \mu\text{g}/\text{m}^3$ ).

Airborne isocyanate concentrations were also monitored from the surface of the paints after “drying” for 24 h and light sanding. The isocyanate levels were found to be below the quantitation levels as expected.

## 4.2 Solvent Vapours

The composition of the solvents is shown in Table 1 with the concentrations ranges as provided by the paint manufacturer [26]. Evaporation rates are listed for some of the components as an indication of the volatility. Air concentrations of the individual components were determined from the analysis of the solvent vapour corresponding to a total concentration of 30 ppm and 90 ppm as measured by the PID.

The total airborne solvent vapour concentrations were measured in a laboratory confined space, on a heated surface ( $57^\circ\text{C}$ ) during roller application. In the confined space of a fume hood (with the fan disabled) concentrations were found to be in the range 30-90 ppm while under the conditions of the CESSNOCK trial, solvent vapour concentrations were approximately 30 ppm in the breathing zone. The composition of the vapour was determined and is presented in Table 4 together with the total vapour concentrations. The evaporation rates listed in Table 4 correlate well with the air concentrations of the solvents.

In the case of Interthane 987 LSALGP, the dominant solvent was xylene as indicated by the analysis of the vapour produced during painting. The xylene vapour concentrations during the CESSNOCK trial were low (17 ppm) compared with the exposure limit (80 ppm). However, there is a potential to exceed the maximum allowable exposure level during paint application in an enclosed space as indicated by the total solvent vapour concentrations (30-90 ppm) measured in the laboratory experiments.

The composition of the solvent vapour from Interthane 864 LSANSP was lower in xylene but also contained butyl acetate and cyclohexanone, both of which emit strong odours. Although the exposure limits for these solvents were not exceeded during the CESSNOCK trial they could potentially be exceeded in an unventilated enclosed space. Furthermore, long-term exposures to these solvents may result in neurotoxic effects but these considerations are beyond the scope of this study.

## 5. Conclusions

Measurements of human exposure to isocyanates and paint solvents during brush/roller application of Interthane 987 LSALGP and Interthane 864 LSANSP were conducted on a RAN patrol boat during a hot day with a slight wind. Concentrations were measured close to the surface of the deck in the open air. These conditions were considered to be conducive to producing airborne isocyanate and solvent vapours. The airborne concentrations of isocyanates, in the breathing zone of the operator, were found to be  $<1/200^{\text{th}}$  ( $<0.1 \mu\text{g}/\text{m}^3$ ) of the maximum allowable concentrations during the application of the paints.

The brush/roller application of the paints in a confined space with air and substrate temperatures  $30^{\circ}\text{C}$  and  $50^{\circ}\text{C}$  respectively, did not generate concentrations of isocyanate vapours in excess of the exposure limits. This is in broad agreement with a study on brush/roller application carried in the UK (presumably undertaken at lower ambient temperatures than this study), where airborne isocyanate concentrations (vapour and aerosol) were found to be below the level of detection during indoor and outdoor applications [19].

On manual sanding of the cured paints (after 24 h curing), airborne isocyanate concentrations (vapour and aerosol) were found to be below the maximum allowable exposure level and below the level of quantitation.

Solvent vapour concentrations, during the application of the paints (under the above conditions) were found to be below the maximum allowable concentrations but these concentrations may be exceeded during paint application in an enclosed space at high ambient temperatures. Furthermore long-term exposures to solvents may result in neurotoxic effects. Given these potential hazards, adequate mechanical ventilation would be required.

Despite the low airborne isocyanate concentrations, personnel should be protected from skin contact with uncured paints.

The above conclusions are relevant to brush and roller applications and do not apply to spray applications.

Table 3: Summary of Isocyanate Monitoring Data

Trial	Application	Paint	Sampling Height (cm)	Isocyanate conc. ( $\mu\text{g}/\text{m}^3$ ) <sup>1</sup>
HMAS CESSNOCK	Roller painted surface (air temp 33°C, surface temp. 57°C)	Interthane 987 LSALGP	70 (personal)	$\leq 0.1$ , $\leq 0.1$
	" "	" "	70 down wind	$\leq 0.1$
	" "	Interthane 864 LSANSP	70 (personal)	$\leq 0.1$ , $\leq 0.1$
	" "	" "	70 down wind	$\leq 0.1$
	Above the paint pot (air temp. 35°C)	Interthane 987 LSALGP	40	$\leq 0.1$
	" "	Interthane 864 LSANSP	40	$\leq 0.1$
Indoor Lab	Roller painted surface (air temp. 30°C, surface temp. 55°C)	Interthane 987 Curing Agent	10	5.2, 7.9
	Brush painted surface (air temp. 30°C, surface temp. 55°C)	" "	15	7.1
	Roller painted surface (air temp. 30°C, surface temp. 55°C)	Interthane 987 LSALGP	10	0.7, 0.6, 1.0, 1.0 <sup>2</sup> , 1.8 <sup>3</sup>
	Roller painted surface (air temp. 30°C, surface temp. 55°C)	Interthane 864 LSANSP	10	1.4, 2.7
	Paint Pot (air temp. 20°C)	Interthane 987 LSALGP	10	0.2
	" "	Interthane 864 LSANSP	10	$\leq 0.1$
Outdoor Lab.	Paint Pot (air temp. 20°C, surface temp. 55°C)	Interthane 987 LSALGP	7.5	$\leq 0.1$ , $\leq 0.1$ <sup>2</sup>
		" "	75	$\leq 0.1$

<sup>1</sup> Sampling flow rate = 1 L/min for 15 min., only HDI detected.

<sup>2</sup> Air Sampling flow rate = 3 L/min. for 5 min.

<sup>3</sup> Air sampling flow rate = 3 L/min., 12 min., LOD = 0.03  $\mu\text{g}/\text{m}^3$ , LOQ = 0.1  $\mu\text{g}/\text{m}^3$ .

Table 4: Solvent Vapour Measurements from Polyurethane Paints

Interthane 987 LSA-LGP				
Conditions	Solvent Total Vapour Conc. (ppm)	Major Components (evaporation rates, butyl acetate = 1.00 <sup>#</sup> )	Conc. (ppm)	TWA (ppm) (NOHSC)
Laboratory, Enclosed space Air temp 30°C Surface 57°C	30-90 (range)			
		Ketones	3.5-10	
		Xylenes (0.7)	17-50	80
		Di(t-butyl) Peroxide	2.5-7.5	
CESSNOCK Trial	30 (mean)		Calculated <sup>*</sup>	
		Alcohols	6.4	
		Ketones	3.5	
		Xylenes (0.7)	17	80
		Di(t-butyl) Peroxide	2.5	-
Interthane 864 LSA-NSP				
Laboratory, Enclosed space Air temp 30°C Surface temp. 57°C	30-90 (range)			
		Butyl Acetate (1)	6.9-21	150
		Alcohols	4.7-14	
		Ketones	3.1-9.3	
		Xylenes(0.7)	2.7-8	80
		Mesitylene	5.2-15.6	25
		Cyclohexanone (0.34)	5.5-15	25
		Di(t-butyl) Peroxide	4.7-14	
CESSNOCK Trial	30 (mean)		Calculated <sup>*</sup>	
		Butyl Acetate (1)	6.9	150
		Alcohols	4.7	
		Ketones	3.1	
		Xylenes (0.7)	2.7	80
		Mesitylene	5.2	25
		Cyclohexanone (0.34)	5.1	25
		Di(t-butyl) Peroxide	4.7	

<sup>\*</sup>Estimated concentrations based on a PID reading of 30 ppm for the solvent mixture.

<sup>#</sup>BP Solve software, Version 3.1 for Windows, April 1998.

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19. ABSTRACT Shipboard and laboratory trials were conducted to determine personnel exposure to airborne solvents and isocyanates during the application, by roller and brush, of 2-pack polyurethane paints. Airborne concentrations in the breathing zones of the operators were found to be <1/200th (<0.1 µg/m <sup>3</sup> ) of the 8 h time-weighted average (TWA) exposure levels for isocyanates during the application of Interthane 987 LSALGP and Interthane 864 LSANSP on a RAN vessel, in the open air, on a hot day with a slight wind. Similarly, brush and roller application of the paints in a simulated enclosed space showed airborne isocyanate concentrations <3 µg/m <sup>3</sup> . The dust produced during light sanding of the polyurethane paint, 24 h after curing, did not show detectable levels of isocyanates. Although it appeared that respiratory protection from airborne isocyanates was not required with brush/roller applications, personnel should be protected from dermal exposure to the liquid paints. There appeared to be a greater risk from paint solvent respiratory exposure than from airborne isocyanates.					